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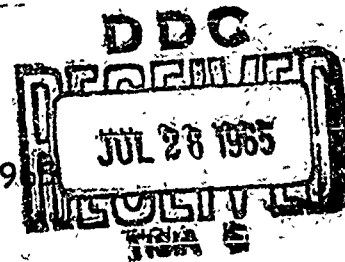
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A CORRELATION OF POLYMERIC
STRUCTURE TO ABLATIVE PROPERTIES

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A CORRELATION OF POLYMERIC STRUCTURE TO ABLATIVE PROPERTIES

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ABSTRACT: The work contained in this report encompasses an attempt to correlate the chemical and physical structure of a polymer with its ablative performance. A broad range of epoxy resins and curing agents were employed as model systems. Various tools such as "alpha rod" testing, thermogravimetric analysis, crosslink density studies, and infra-red spectroscopy were used in making this correlation.

The epoxy novolac type resin performed the best of all the epoxy resins in the "alpha rod" oxy-acetylene torch test while nadic methyl anhydride performed as the best curing agent for epoxy resins under these ablative conditions. The use of a refractory filler such as SiO_2 was found to be necessary for good performance. The mechanism through which this filler aids the ablative properties of materials is explained with the help of photomicrographs.

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WHITE OAK, MARYLAND

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A CORRELATION OF POLYMERIC STRUCTURE TO ABLATIVE PROPERTIES

This report encompasses the first of three phases of the High Temperature Ablating Materials Program. The work and conclusions reported here should facilitate the synthesis of new organic polymers specifically designed to perform in hyperthermal environments. The work was conducted under Bureau of Naval Weapons Task RRMA 03-043/212-1/RO07-04-01, Problem Assignment No. 74-4, High Temperature Ablating Materials.

Many of the materials discussed in this report were obtained from commercial sources. Their evaluation by the Laboratory in no way implies Navy endorsement for their high temperature usage. Neither is this consideration of a material by the Navy to be used for promotional purposes. There is no implication intended that other materials might not have performed as well as those selected for these studies.

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By direction

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INTRODUCTION

During the past ten or fifteen years, the aerospace industry has placed strenuous demands upon our inventory of high temperature organic polymers. These polymers have served in a variety of ablative areas such as in nose cones, rocket cases and nozzle sections, and heat shields for re-entry vehicles. These polymeric materials are not ideal but they do perform their function adequately, for the most part. However, the demands of our missiles with their ever increasing energy limits, will tax the performance of our present day ablative insulators to the point of failure.

A great deal of ablative testing of candidate insulator materials has been performed in the past several years. A wide spectrum of polymeric materials have been screened alone and in combination with varied percent and type of fillers in a number of different ablative environments. As a result, the more promising materials were tested further under the more exacting conditions of their proposed use, and were finally chosen as acceptable or discarded.

However, performance-wise, we have almost completely exhausted our readily available polymeric insulators and combinations thereof. To further increase ablative insulation efficiency, we must synthesize new polymers. To do this we must have a better insight into what a good ablative insulator is structurally composed of. Therefore, it is the purpose of the work reported herein to correlate the chemical and physical properties of organic polymers with their ablative performance.

It has been generally believed that organic polymers containing a large percent of aromaticity and a high crosslink density would give the best ablative performance. This is exhibited by the phenolic resins. However, several deviations from this so-called "rule" were found in the work reported here.

This program has been divided into three main phases. The first phase of the work is contained in this report. It involves research on the more common epoxy resins commercially available to relate structure to thermal stability and ablative performance. (Epoxy resins were used as model compounds.) Various curing agents were also used to determine the dependence of epoxy resins on their curing agents in this same regard. The second phase encompasses a study of the more exotic epoxy resins with novel structures including the family of epoxy novolacs. This second phase will terminate the research on commercially available epoxy resins. Based on the conclusions derived from Phase I and Phase II data, a syntheses program (Phase III), will be undertaken. This synthesis will be aimed at integrating in one polymer as many of the structural components as possible which will give a good ablating material.

Research was performed on the model epoxy compounds described herein by means of thermal gravimetric analyses, infrared spectroscopy and "alpha rod" testing. This report contains the data from these tests, its meaning and its use towards the correlation of the chemical and physical properties of a polymer with its ablative properties.

THEORETICAL

General

In order that the purpose of this program be achieved it was essential that a model system be employed. Toward that end the family of epoxy resins was chosen. Epoxy resins serve well as model compounds for a number of reasons. First, a wide variety of resin structures is possible, ranging from the highly aromatic and highly functional novolac type to the conventional bisphenol-A-epichlorohydrin condensate to the cyclic aliphatic type to the straight chain aliphatic type and so forth. In short, an epoxide resin can be made from virtually any type of chemical structure. Also, the curing agents employed with epoxy resins offer versatility in regards to mode or type e.g., a polyamine resin will result from the use of an amine curing agent or a polyester type resin as a result of an anhydride cure or polyether type resin as a result of a catalytic cure with a tertiary amine. The curing agents also offer versatility in that they may be aromatic, straight chain aliphatic, cyclic aliphatic, heterocyclic, and so forth.

Second, and most important, you can determine with a good degree of certainty, the chemical and physical properties of the final polymerized structure. Knowledge of the final structure is essential for the purpose of this program and is arrived at by: 1) knowing the initial resin and curing agent structure, 2) knowing in detail, the reactions to be expected during the cure of the resin, 3) chemical end-group analysis to determine the percent conversion of epoxide, 4) crosslink studies to determine the crosslink density, 5) infrared spectrographic analysis to determine completeness of conversion of epoxide and consumption of curing agent.

Third, the epoxides were chosen as the model system because they are relatively easy to work with. Last but by no means least, the epoxides have shown some promise already in aerospace applications such as heat shields for re-entry vehicles. Therefore, although realizing that better ablators could be prepared for near-immediate use by optimizing filler-polymer combinations of existing aerospace materials, it was felt that the conclusions derived from this study of model compounds would be more valuable over the long run.

Epoxy Resins Used in Phase I

The choice of epoxy resins was designed to explore the structural spectrum of epoxy resins in regards to the aims of this program.

In Figure 1, the idealized structure of an epoxy novolac is represented in formula 1. This novolac, it was predicted, would give the best ablative performance due to its high degree of aromaticity and functionality.

Formula 2 of Figure 1 again represents an idealized structure of a resin that is actually composed of various isomers and homologues. This compound looked interesting because its high degree of aromaticity and functionality is equal to that of many of the novolacs.

The "standard" epoxy resin, the bisphenol-A-epichlorohydrin condensate is represented by formula 3 in Figure 1. This resin is the "workhorse" of reinforced plastics. A close look at its thermal stability and ablative performance was desired so that we might have a "standard" with which to compare future work. Our final choice of resin was a purely aliphatic epoxy resin with low functionality as represented by formula 4 in Figure 1.

Curing Agents Used in Phase I

The choice of curing agents was designed to cover the range of curing agents from di and trifunctional anhydride to aliphatic and aromatic amines. The curing agents are represented in Figure 2. Ideally, each curing agent would be used with each epoxy resin in Figure 1. However, due to cure difficulties such as insolubility and high exotherm, this was not always possible.

Mechanism for Amine Cure of Epoxy Resins

The three reactions which are possible when curing an epoxy resin with an amine are shown in Figure 3. The nucleophilic attack by the nitrogen atom on the epoxide carbon to form secondary and tertiary amines is the main reaction (Fig. 3, No. 1 and No. 2) as shown by Wynstra, et al (ref. (a)). Reaction No. 3, Figure 3 is an etherification type reaction which can occur between epoxide groups and hydroxyl groups. These are formed for example in reactions (1) and (2). However, reaction No. 3 seldom occurs below 200°C when uncatalyzed. Tertiary amines can catalyze this reaction at much lower temperatures but the tertiary amines formed in reaction No. 2 are too sterically hindered and immobile to efficiently catalyze reaction No. 3. The hydroxyl formed in No. 1 and No. 2 can aid the amine epoxide reaction by hydrogen bonding to the epoxide oxygen and thereby aiding the opening of the ring. Therefore, reactions No. 1 and No. 2 are by far the main reactions almost to the exclusion of reaction No. 3.

Mechanism for Acid Anhydride Cure of Epoxy Resins

The mechanism of cure of epoxy-anhydride systems is generally more complex than for epoxy-amine systems. The three major competing reactions in epoxy-anhydride systems are given in Figure 4. The anhydride ring is somewhat unreactive in regards to epoxy. Therefore, in reaction No. 1,

the anhydride reacts with an hydroxyl group to form the monoester and the monoacid. Then, the monoacid may react with an epoxide to give the diester and an hydroxyl with which to continue the polymerization as in reaction No. 1.

However, reaction No. 3 assumes importance in the anhydride cure of epoxy resins as noted by Dearborn, et al (ref. (b)). The acid catalyzed etherification reaction results in a polyether whereas the anhydride-epoxy reaction results in a polyester. Therefore, the properties, both thermal and mechanical, of the cured polymer will depend upon what extent this reaction (No. 3), competes with reactions No. 1 and No. 2.

In the acid anhydride cure of the epoxy resins of this program, 85% of the stoichiometric amount of curing agent was used. This allows for 15% etherification. It would have been prohibitive timewise, to optimize the polyether-polyester ratio for each system and therefore the 85% stoichiometric amount of anhydride was chosen.

Filler

This program is ultimately concerned with the development of a better organic ablator than is currently available. However, it was felt that some of the epoxide models used might ablate so quickly in the "alpha rod" test that differences in ablation rate would not be discernible. Therefore, it was decided to test both filled and unfilled specimens.

The choice of filler was dictated by a variety of factors which include handling, as well as its past use in ablative composites. A 20% loading of finely ground (+ 100 mesh) SiO_2 was used throughout along with 5.0% (of the 20% filler) TiO_2 . The thought behind the TiO_2 was that it might possibly reduce radiative heat by partially reflecting it. As we shall see later however, it proved to be of little if any value.

EXPERIMENTAL

The resins and curing agents given in Figures 1 and 2 were mixed and cured according to set schedules. As mentioned before, due to difficulties in solubility, exotherm and so forth, not all curing agents were used with every epoxy resin. The stoichiometric amount was used for amine curing agents. In the case of anhydride curing agents 85% of the stoichiometric amount was used for reasons outlined above in the theoretical section. Postcures up to two days and 225°C were imposed upon the systems depending on the resin and curing agent involved.

As a rule, 200 gm quantities of resin were used. After mixing the curing agent and resin, castings were made in rod shapes approximately one inch by five inches. These rods were then either machined into "alpha rods" or ground into powder and sieved (+ 60 mesh) for the various experiments.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was one of the two major tools used in this program. From TGA X-Y plots, one can readily observe the thermal stability of a polymer. Also, it was hoped that some correlations between the TGA curve of a polymer and its ablative performance could be made. As we shall see later on, this was possible to some extent.

The TGA apparatus used in this program was constructed around an Ainsworth Model RU-AV-2 semimicro vacuum recording balance. The apparatus and its operational characteristics are given in reference (c). A picture of the apparatus is given in Figure 5.

Generally, twenty milligram powdered samples, (+ 60 mesh - 80) were employed in the TGA. The entire system was put under a vacuum at approximately 0.05 mm Hg and a heating rate of 5°C/min was used. The X-Y TGA plots shown in this report were redrawn from the tracings of the TGA apparatus's two-pen Bristol recorder.

"Alpha-Rod" Testing

The "alpha-rod" test constituted the second major tool of this program. The "alpha rod" and the testing thereof in the oxyacetylene torch facility is well covered experimentally and theoretically in references (d), (e) and (f). The "alpha rod" oxy-acetylene torch apparatus is shown in Figure 6. Briefly, the "alpha rod" which is 3/4 inch in diameter and possesses a thermocouple imbedded 3/8 inch behind its front face, is fed forward through the heat shield at a rate equal to that of its ablation rate. The position of the front face remains fixed, flush with the end of the flame shield. Thus conditions of constant one-dimensional heat flux exist at the front face of the specimen. The ablation rate is recorded as well as its temperature history. The heat flux encountered by the front face of the "alpha rod" is approximately 58 cal/cm² sec. Fully realizing that there are a host of ablative conditions and environments with materials performing differently in each one, the above described ablation test was chosen as being an average ablative condition although possibly not duplicating any particular one.

Infrared Spectroscopy

Infrared spectroscopy was used as a means of verifying the structure of starting materials as well as to indicate degree of conversion of epoxide. Also IR was used to determine whether there was any residual free anhydride after the post cure of an epoxy anhydride system. Selected chars taken from "alpha rods" were examined using the attenuated total reflectance technique with the IR. The infrared machine used is a Perkin-Elmer Model No. 337 Grating Infrared Spectrophotometer.

Crosslink Density

A crosslink density study was conducted on all the unfilled resin systems given in this report. The percent swelling in solvent vapor

technique was used as outlined by Dannenberg and Harp (ref. (g)). By this method, the greater the increase in weight of a powdered resin system the lower is its crosslink density. The value determined by this method is relative and not absolute. However, it is a simple and reproducible method of determining crosslink density. The purpose of this study was to try to correlate crosslink density with ablative performance of the resin systems.

RESULTS

Thermal Gravimetric Analysis

The TGA results are given in both graphical and tabular form in Figures 7 through 13 and Tables 1, 2 and 3. The graphs show general trends whereas the tables give more detailed information on the thermal degradation of a polymer system.

Figure 7 shows the most thermally stable resin system of each epoxy resin studied in Phase I. Also a phenolic was added for comparison. The general trend shown here is that which prevails throughout all the epoxy resin systems in this report, that is, the aliphatic epoxy resins performed poorly, bisphenol-A type resins performed better and the novolacs performed the best. Except for the aliphatic resin, all systems shown in Figure 7 had only a 10% weight loss in the region of 400°C.

Figure 8 shows the bisphenol-A type resin systems. All curves are similar with the exception of NMA-Epon 828 curve which will be explained later. Figure 9 shows Epon 1031, cured with various anhydrides and amines. It is interesting to note the wide range of temperatures at which initial degradation takes place and yet all the systems seem to converge at 550 to 600°C to one curve.

Figure 10 shows the widest spread of values of any epoxy resin in this program. Initial degradation varies over a range of 150°C depending upon curing agent used. Note the fairly wide temperature range over which the NMA cured specimen decomposes as opposed to the DADPS cured specimen. Also, again note the step curve of the NMA cured specimen.

Tetrahydrophthalic anhydride (THPA) proved to be one of the poorer curing agents as is shown in Figure 11. The mode of decomposition of each resin with THPA seems similar. Only after 60% weight loss does a major difference appear. After 60% weight loss the resins seem to fall out on a plateau indicative of the degree of aromaticity which each possesses, Epon 828 having the lowest and Epon 1031 the highest.

In Figure 12 we see the ability of DADPS to produce thermally stable polymers. However, once thermal degradation is initiated, the polymer systems decompose rapidly. Again note the superiority of the novolacs over the bisphenol-A type resin.

In Figure 13 we again see the effect of NMA on the various resins. All curves are similar, although displaced to the right or left depending on their aromaticity and functionality. All have the characteristic plateau effect of NMA cured epoxy resins in the region of 225 to 300°C. Again note the superiority of the novolacs over the bisphenol-A type resin in the area above 60% weight loss. This will be discussed later.

"Alpha Rod" Testing

The results of the "alpha rod" tests are given in Table 1 along with the percent char as determined by TGA, crosslink density and specific gravity. The ablation rates of most of the epoxy systems were high for the most part falling in the range of 9.0 to 13.8 mils/sec. However, the epoxy novolacs in combination with NMA and 20% filler, performed well with ablation rates of 1.4 and 2.8 mils/sec for Epon 1031 and RDR-701, respectively. There was little difference between the filled and the unfilled specimens of the bisphenol-A type. However, almost a tenfold decrease in the ablation rate occurred for some of the filled novolac-type resins over their unfilled counterparts. There was a marked improvement in the bisphenol-A type resin by the addition of 30% filler as opposed to the specimens with 20, 10 and 0% filler.

Crosslink Density

The crosslink density of the resin systems is given in Table 1. Crosslink densities were widely scattered but a given value was generally reproducible within 1% of the original value. DADPS and MPDA generally gave the highest crosslink density for any given resin system and in particular was greatest for the novolac RDR-701. NMA (methyl-bicyclo (2.2.1) hept-5ene-2,3-dicarboxylic anhydride) cured specimens had the lowest crosslink densities.

DISCUSSION OF RESULTS

Thermalgravimetric Analysis

Discussion on the TGA will revolve around Tables 2, 3a and 3b. The material in these tables was taken from the TGA curves of the various resin systems (Figs. 7 thru 13 inclusive).

In Table 2, we see that in general, all the resin systems composed of the bisphenol-A type epoxy (Epon 828) have similar values and hence similar thermal decompositions. Therefore we can assert as a generalization that the standard bisphenol-A type epoxy resins exhibit thermal properties which are independent of their curing agent except in the initial stages of degradation.

Upon further perusal of Table 2, we note that diaminodiphenyl sulfone appears to give the most thermally stable materials with all three resins, judging by temperatures at which a 10% weight loss has occurred. Somewhat

paradoxically, note the temperature at which the NMA cured resins have lost 10% of their weight. In every case, these systems started degrading at a considerably lower temperature than any of the other systems, yet these resins ablatively performed better by far than any of the other systems.

In Table 3a the same observations noted above are true. DADPS cured systems give the lowest percent of the weight loss at 350° and NMA cured systems give the highest percent weight loss at 350°C. At 450°C the TGA curves of the DADPS and NMA cured systems approach one another and in some cases cross.

A different portrayal of the TGA data is given in Table 3b. From this type of data a somewhat generalized correlation can be made between TGA data and ablation rate data. This correlation is only valid for polymers degrading in the range of 200 to 600°C since this is the only area in which there is sufficient data at this time. In general, for a polymer system to perform well as an ablator, it's TGA weight loss from 5.0 to 75.0% should occur over a temperature range greater than 200°C. Also, the temperature range from 70.0 to 80.0% weight loss should be greater than 200°C. The fact that the first range is large indicates that the resin degrades slowly and efficiently over a long range such as NMA cured specimens and as opposed to Epon 828 + DADPS which undergo major degradation over a small temperature range. The second range (70.0 to 80.0%) should be large also since this would indicate a small slope which was caused by the formation of a thermally stable char.

'Alpha Rod' Testing

As was noted under results, the ablative performance of these epoxy resins, whether filled or unfilled, was poor except for the filled, NMA cured novolac and Epon 1031. These latter resin systems performed well and developed a strong char. It is proposed that this char is a silicone-carbon crosslinked polymer formed by the reaction of the epoxide polymer with the SiO_2 filler at temperatures upwards of 3000°C in the oxy-acetylene torch facility. This char decreases in density but increases in strength as you proceed outward from the virgin polymer-char interface. Figures 14 through 16 are photomicrographs of various chars from the "alpha rods" used in this program. The magnification of the photomicrographs is approximately 6 X.

Figure 14a is the front view of an Epon 1031 + NMA + 20% silica. This char was formed during the entire duration of the run, (i.e., until the heat source reached the thermocouple imbedded 3/8 inch from original front face.) Note the cracks irregularly spaced on the surface. These cracks are necessary as they allow the diffusion of gaseous degradation products from the underlying virgin polymers. These gases also break down further on the myriad hot char surfaces through which they pass, thus absorbing more heat.

Note in Figure 14b which is the char surface at the virgin polymer-char interface of the same specimen, that the cracks are still present although the overall view of the char is of a denser one.

Figure 14c is a side view of the same char, again note the cracks.

Figure 15a is a photomicrograph of the same type of char but a different specimen. This front view exhibits an abundance of cracks through which the degradation gases may pass.

The back view of this same specimen is shown in Figure 15b. Note here, that there are virtually no cracks in the char structure. Therefore the degradation gases, although they could diffuse through the char to some extent, they could not be liberated fast enough to prevent a blow off of the char by the pressure of these gases.

Figure 15c is a sideview of this same specimen. Note how it is smaller than the previous char due to premature blow off. Note also the trail off of cracks and the densification as the virgin polymer-char interface is approached.

A very dense char is shown in Figure 16a. This is formed by the polymer system Epon 828 + NMA + 30% silica. However, there are only one or two cracks of any size to allow degradation gases to escape. Also note in Figure 16b, the back view of the same char, which is almost free of cracks and very dense. Therefore due to the entrapment of degradation gases beneath the char, blow off occurred before the char had reached 1/16" in thickness.

An excellent example of what happens if there is no filler present is shown in Figure 16c. This is the same material as was used in Figures 14 and 15 except the filler has been deleted. As can be seen, the char is very flakey and soft. Continual spallation of this char occurred in the gas velocity range obtained with the oxy-acetylene torch. As mentioned before, the ablation rate of this unfilled specimen is about ten times greater than its 20% filled counterpart.

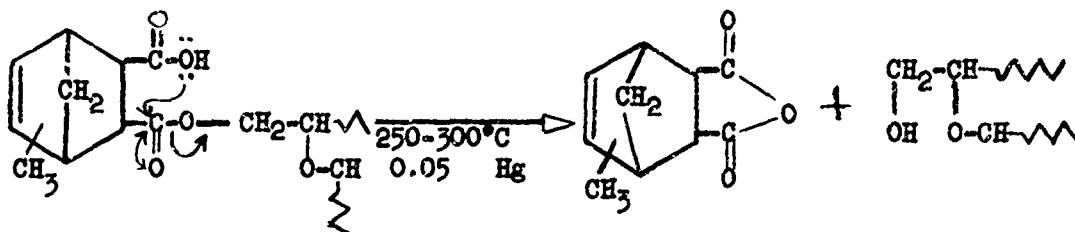
Crosslink Density

After reviewing the crosslink density and other data in Table 1, there seems to be no direct link between crosslink density and ablative performance. The NMA cured Epon 1031 has the lowest crosslink density of any of the resin systems yet gives the best ablative performance. RDR-701 and Epon 1031 cured with MPDA have the highest crosslink density yet their ablative performance is relatively poor. Therefore, it does not seem possible to establish a correlation between crosslink density and ablative performance at this time.

NMA Cured Epoxy Resins

A study of the unusual stepwise degradation mechanism of methyl-bicyclo (2.2.1) hept-5ene-2,3-dicarboxylic anhydride (NMA) was initiated after NMA-cured epoxides showed promise as good ablative performers. It is essential to know the degradation mechanism since this controls the erosion rate to a large extent. Once the mechanism is understood, it may be possible to increase or decrease the erosion rate of a material by altering the percent of NMA or its basic structure slightly.

Infrared work shows that most NMA cured specimens have no carbonyl frequencies at 1770 cm^{-1} or 1850 cm^{-1} indicating that almost all anhydride rings have been broken. However, it is possible that some monoacid-ester remains after cure and undergoes the following reaction in the $250\text{-}300^\circ\text{C}$ range.



The NMA would volatilize off as soon as it was split out under these conditions. The residual free acid is caused by an incomplete cure. This may be due to steric or electronic effects of the methylene bridged bicyclo structure of NMA in the partial inhibition of the formation of diester. Decarboxylation also may occur but only as a secondary effect after the NMA has been split out of the polymer molecule.

CONCLUSIONS

Epoxy novolac and the Epon 1031 type resins are the most promising candidates for good ablative resins. Their superiority appears to be due to their high degree of aromaticity and functionality.

Standard epoxy resins (i.e., bisphenol-A-epichlorohydrin condensate) are inferior as thermally stable and ablative materials. Their performance, which is to a large extent independent of the curing agent can be made marginal only by optimum concentrations of curing agents, fillers and/or plasticizers. Its low aromaticity and functionality are not sufficient.

Strictly aliphatic systems such as Epon 871 and TETA are inferior materials in regards to thermal stability and ablation. Such curing agents as diaminodiphenyl sulfone and metaphenylenediamine which give good thermal stability to a resin system do not necessarily give it good ablative characteristics.

The use of a filler such as SiO_2 is necessary for good ablative performance. A crosslinked silicone-carbon polymer is believed to be formed by the reaction of certain epoxy novolac systems with the silica filler in the oxy-acetylene torch test.

RECOMMENDATIONS

Further investigation of the epoxy novolacs should be undertaken. A fairly wide variety of novolacs are known. Optimization of currently available novolacs would give increased knowledge in the correlation of chemical and physical properties with ablative performance.

Continued research into the degradation mechanism of NMA cured epoxies should be fruitful from a number of points of view.

Investigation of polyethers formed by the catalytic homopolymerization of epoxides brought about by such compounds as $\text{BF}_3\text{NH}_2\text{C}_2\text{H}_5$ should also be undertaken.

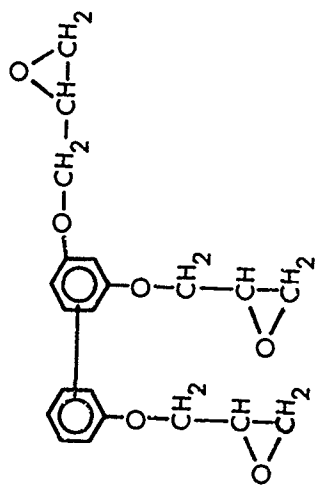
A study of the effects of other bridged bicyclo anhydride curing agents should be interesting also. A whole family of curing agents of this type is possible using the Diels-Alder reaction.

Various cyclic aliphatic and heterocyclic epoxides should be investigated as to their ablative performance.

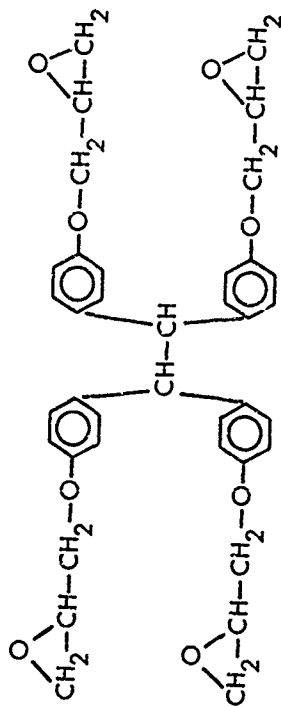
ACKNOWLEDGEMENTS

The author wishes to acknowledge the beneficial and timely suggestions of Mr. F. J. Koubek.

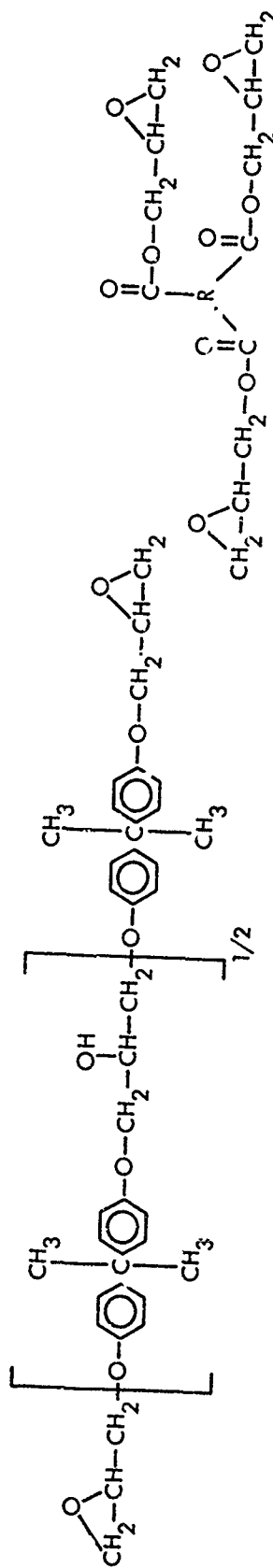
He also wants to express his thanks to Mr. William McLean for his aid in the "alpha rod" testing of the specimens.



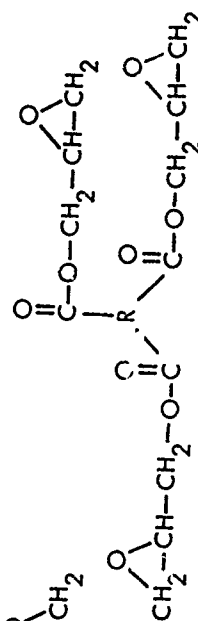
RDR - 701
(Formula 1)



EPON 1031
(Formula 2)

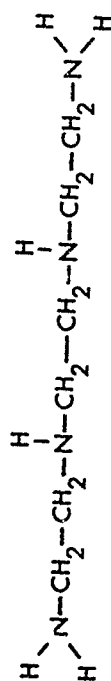


EPON 828
(Formula 3)

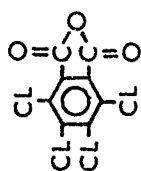


EPON 871
(Formula 4)

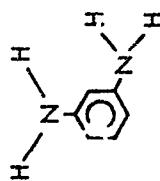
FIG. 1 EPOXY RESINS USED IN PHASE I OF HIGH TEMPERATURE
ABLATING MATERIALS PROGRAM



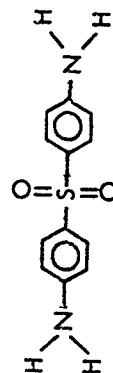
TETA Triethylenetetramine
(Formula 4)



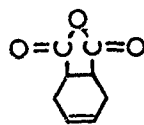
TCPA Tetrachlorophthalic Anhydride
(Formula 5)



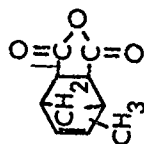
MPDA Meta-Phenylenediamine
(Formula 6)



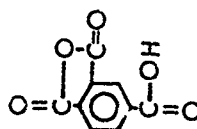
DADPS 4-4' Diaminodiphenyl Sulfone
(Formula 7)



THPA Tetrahydrophthalic Anhydride
(Formula 1)



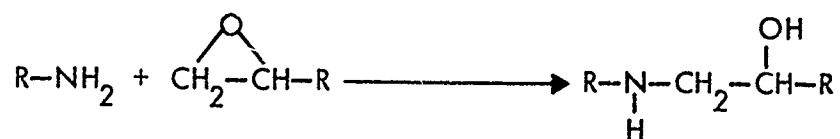
NMA Nadic Methyl Anhydride
(Formula 2)



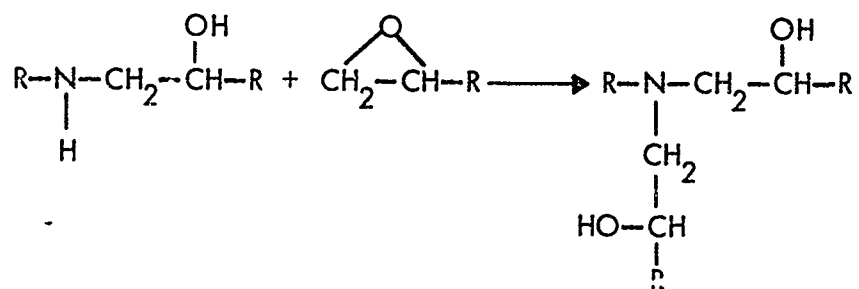
TMA Trimellitic Anhydride
(Formula 3)

FIG. 2 CURING AGENTS USED IN PHASE I OF HIGH TEMPERATURE
ABLATING MATERIALS PROGRAM

1.) Formation of Secondary Amine



2.) Formation of Tertiary Amine



3.) Etherification

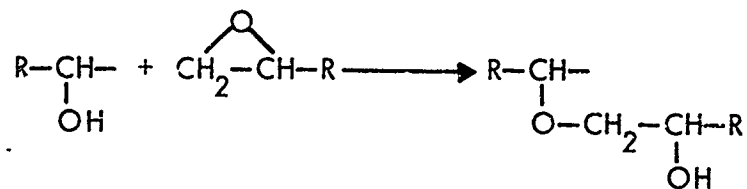
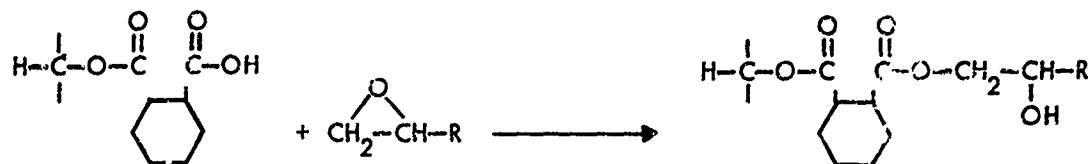


FIG. 3 MECHANISM FOR AMINE CURE OF EPOXY RESINS

1.) Formation of Monoester



2.) Formation of Diester



3.) Etherification reaction

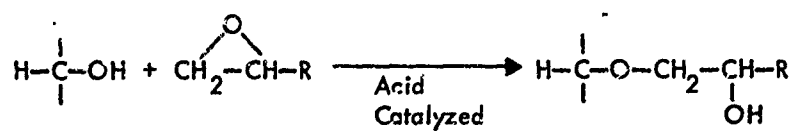


FIG. 4 MECHANISM FOR ACID ANHYDRIDE CURE OF EPOXY RESINS

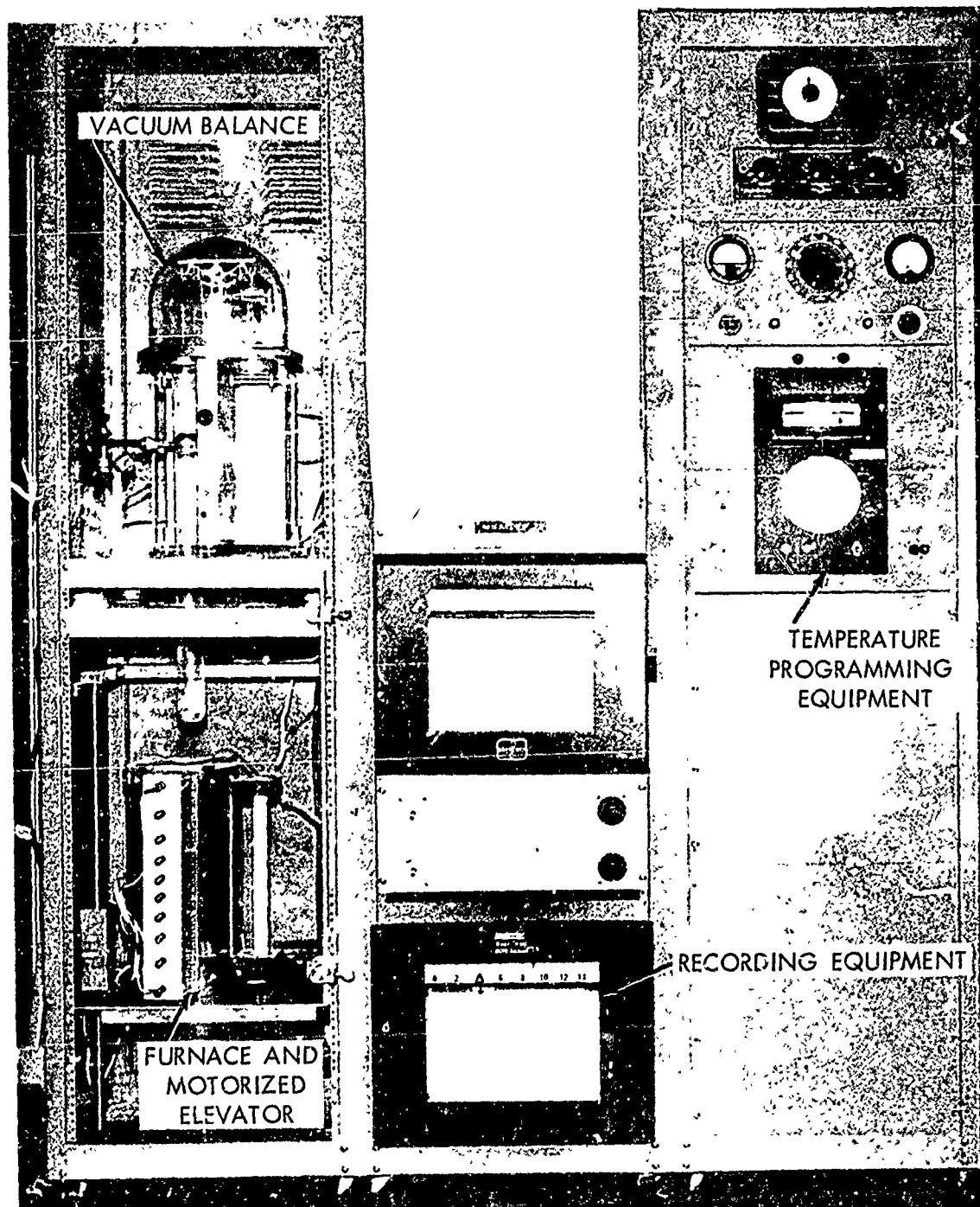


FIG. 5 THERMAL GRAVIMETRIC ANALYSIS APPARATUS

NOLTR 65-50

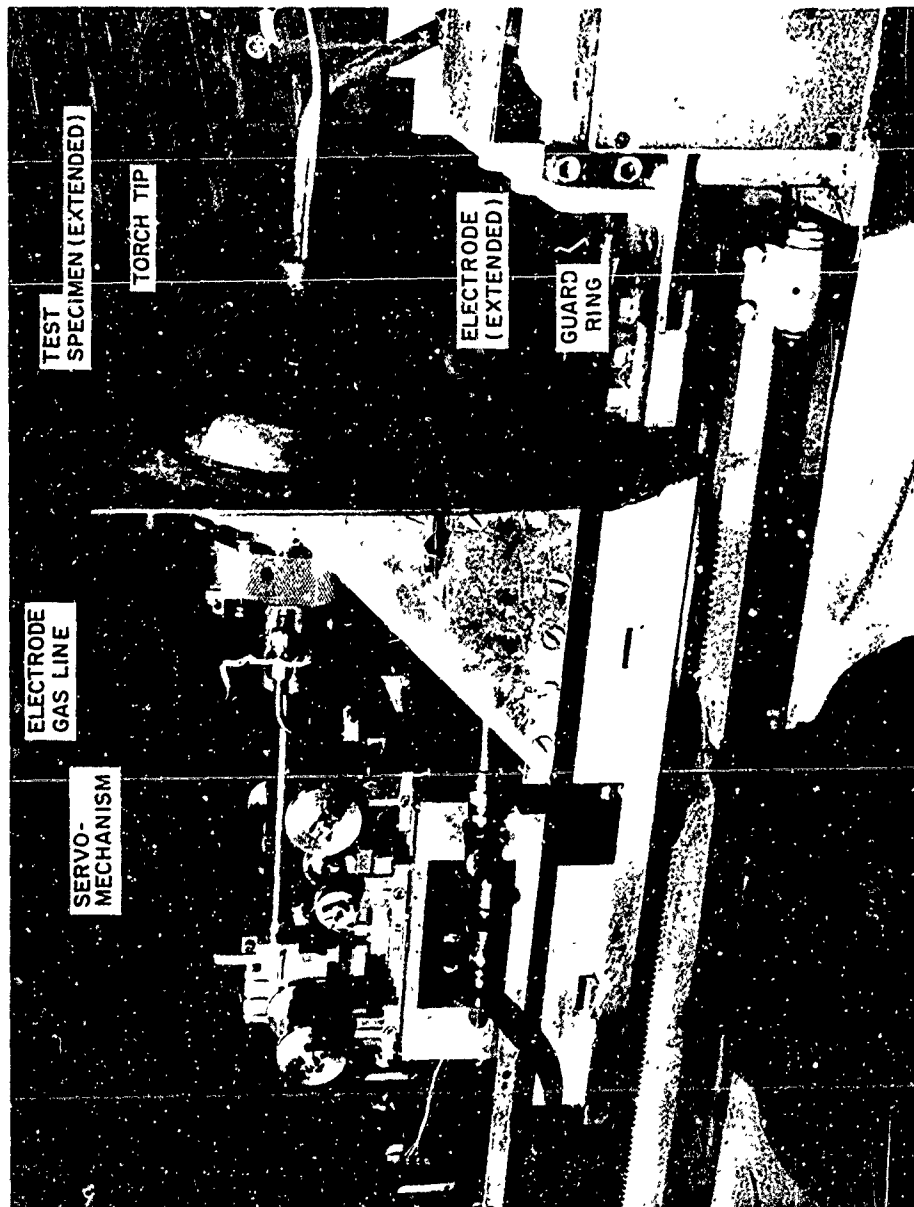


FIG.6 GENERAL VIEW OF AUTOMATIC FEED DEVICE AND OXY - ACETYLENE BURNER

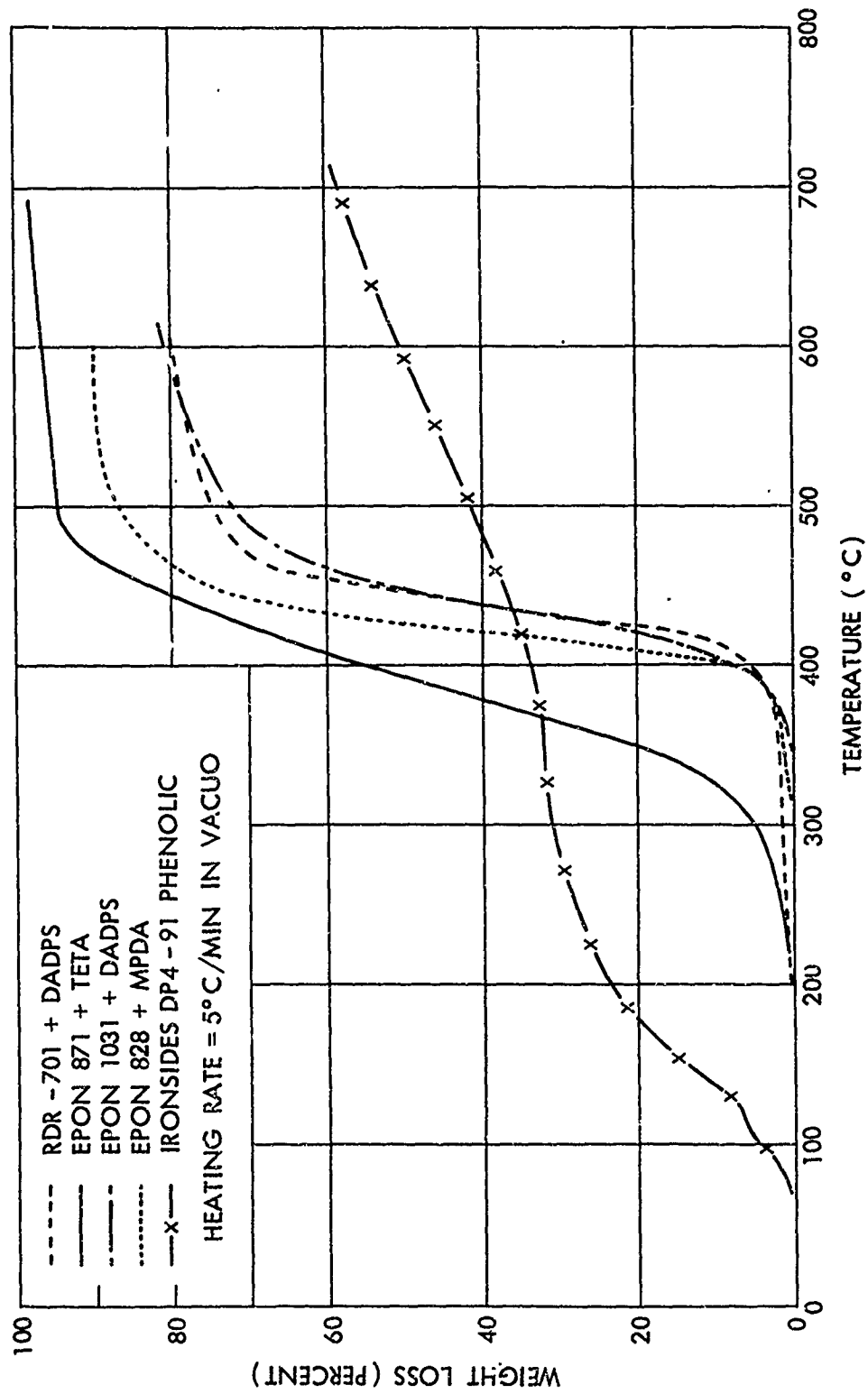


FIG. 7 MOST THERMALLY STABLE SYSTEMS OF PHASE I EPOXY RESINS

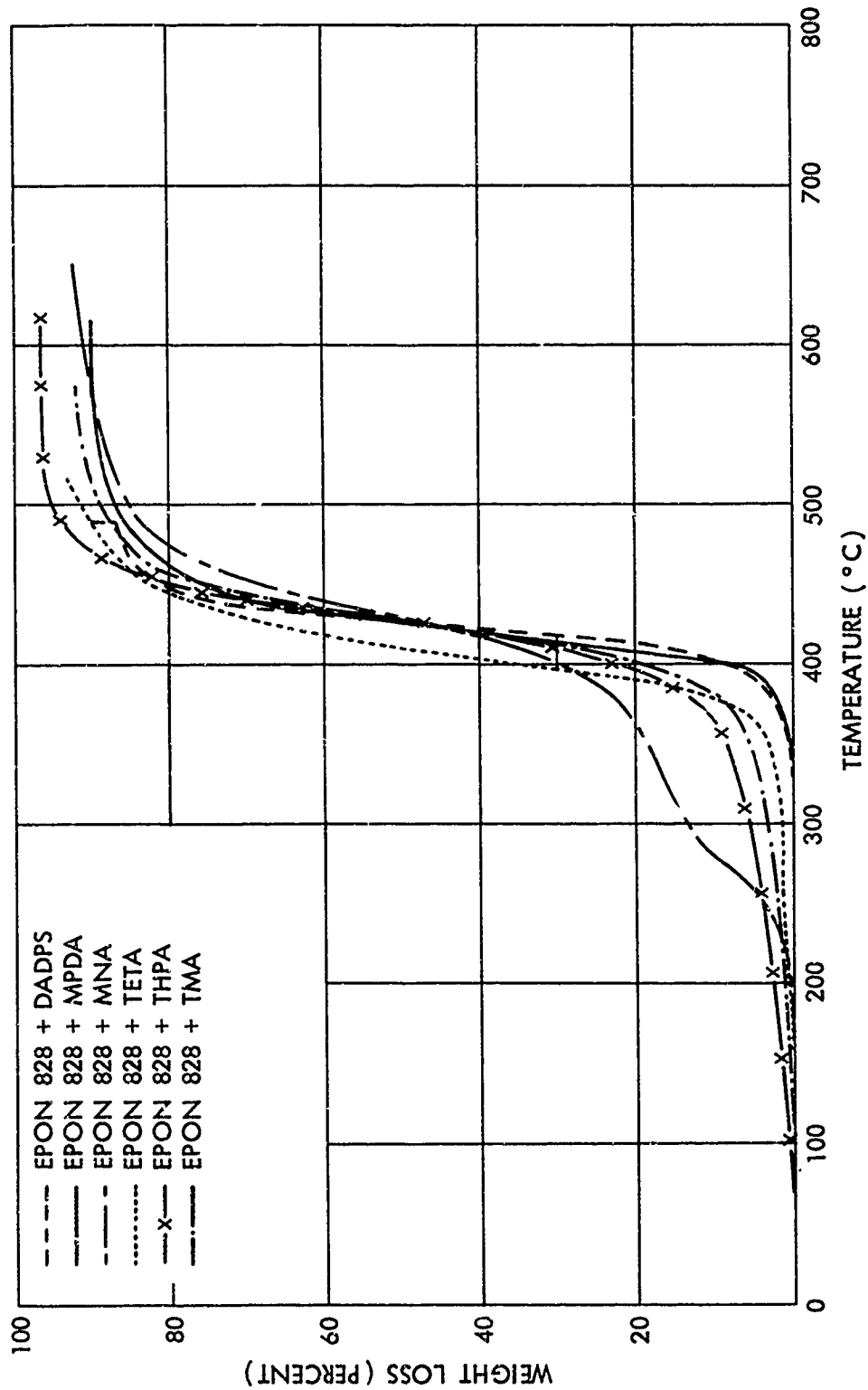


FIG. 8 EFFECT OF CURING AGENTS ON THERMAL STABILITY OF EPON 828 (BISPHENOL-A TYPE)

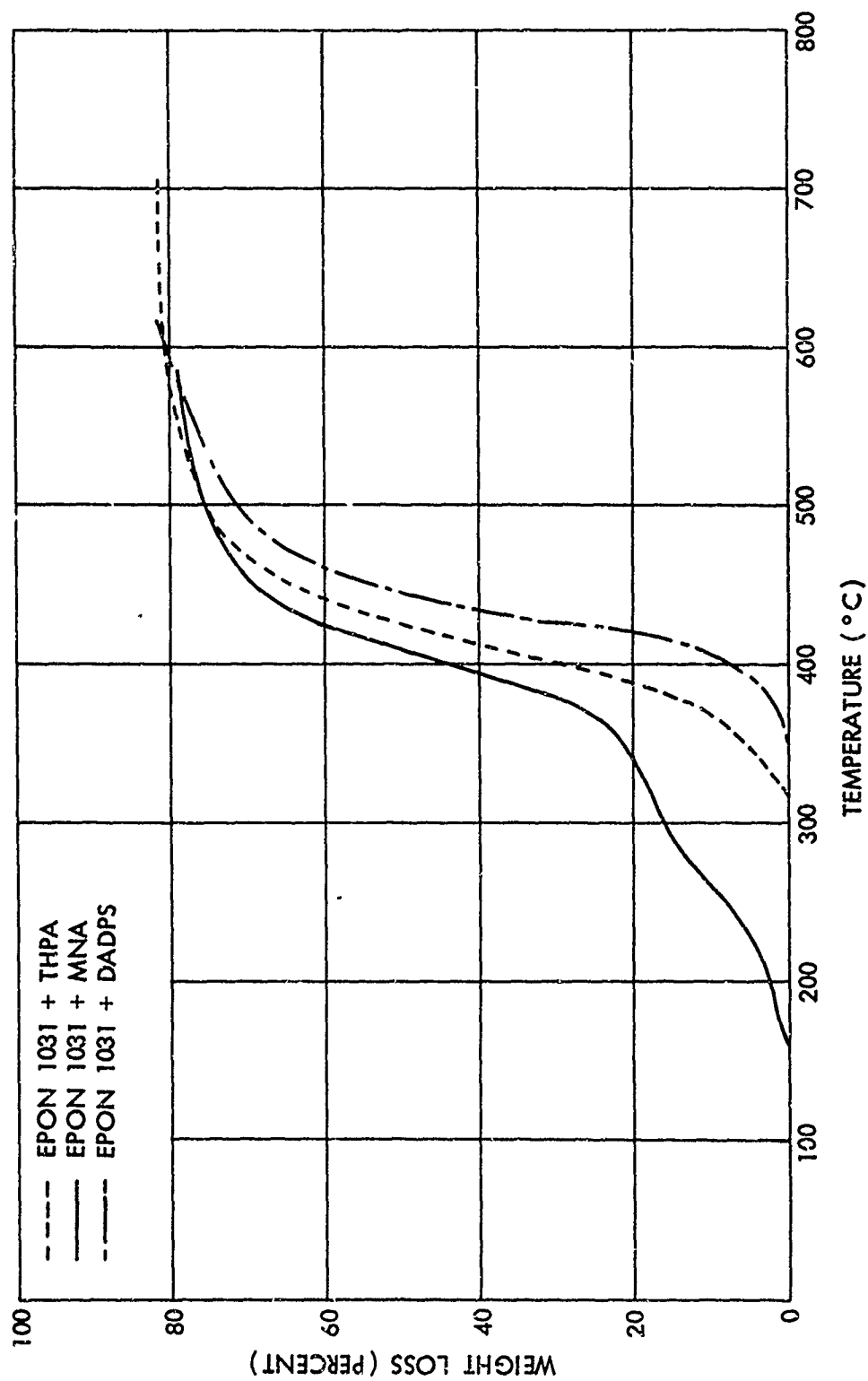


FIG. 9 EFFECT OF CURING AGENTS ON THERMAL STABILITY OF EPON 1031

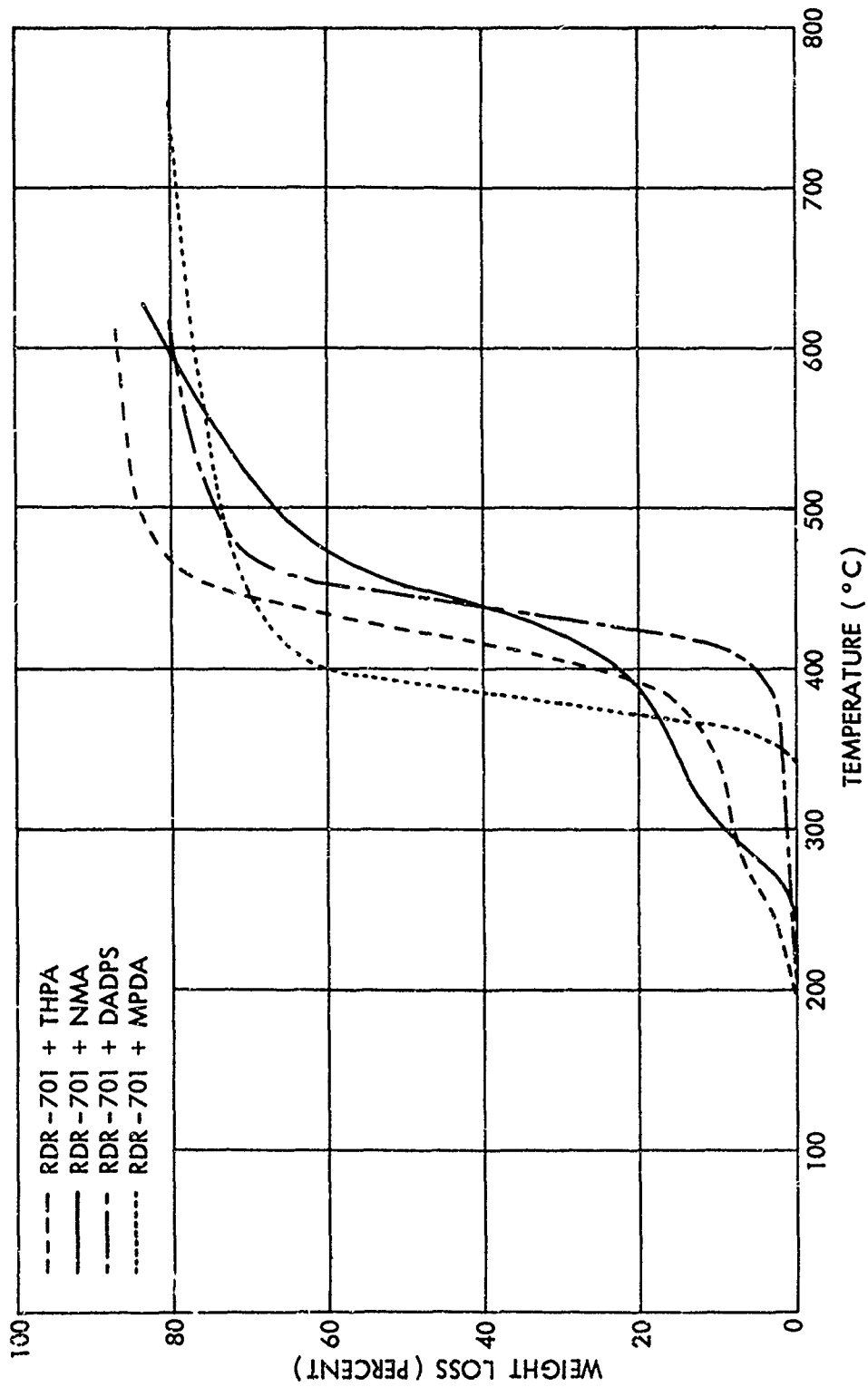


FIG. 10 EFFECT OF CURING AGENT ON THE THERMAL STABILITY OF RDR-701 (NOVCLAC-TYPE)

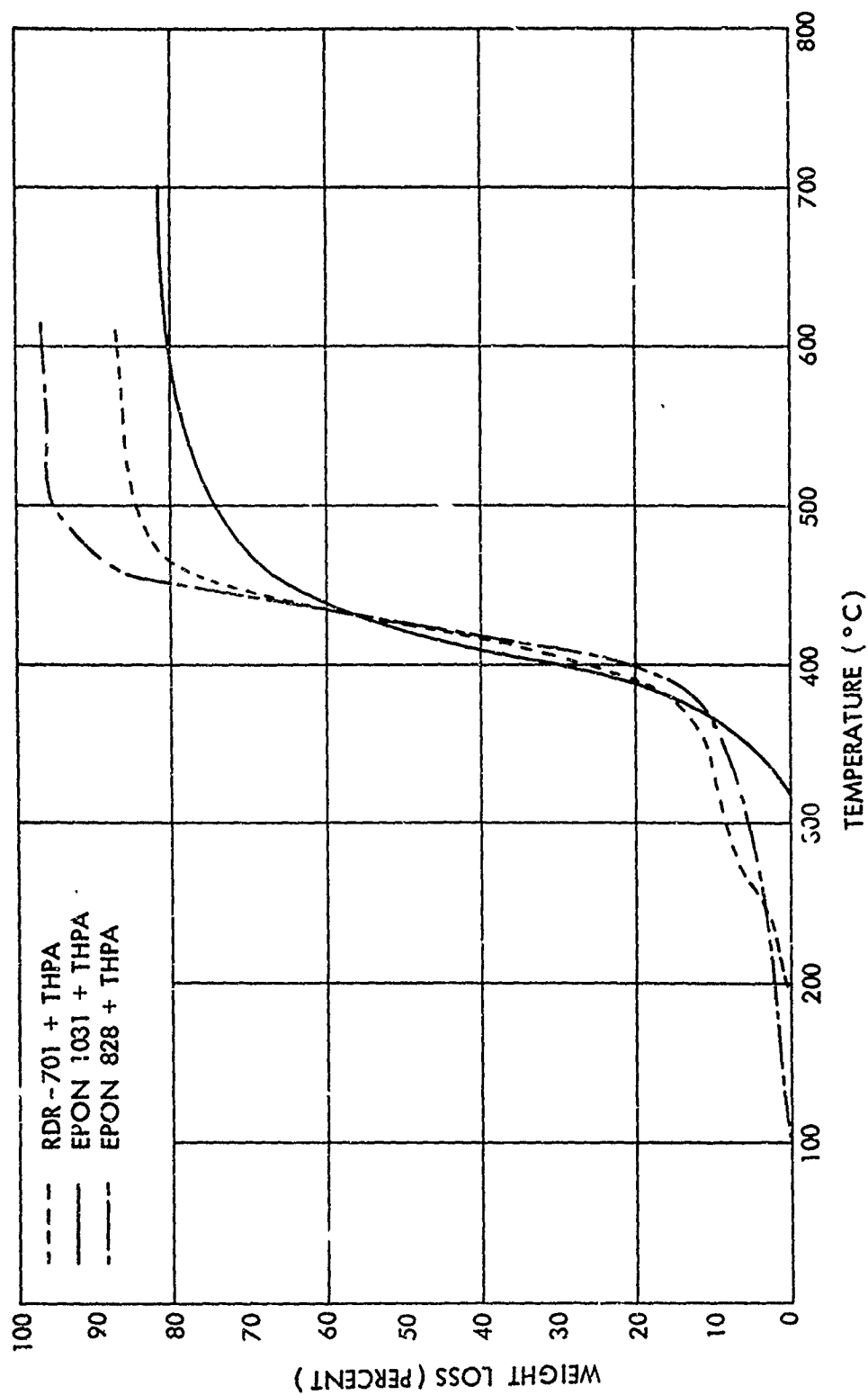


FIG. 11 EFFECT OF TETRAHYDROPHTHALIC ANHYDRIDE ON THE THERMAL STABILITY OF SEVERAL EPOXY RESINS

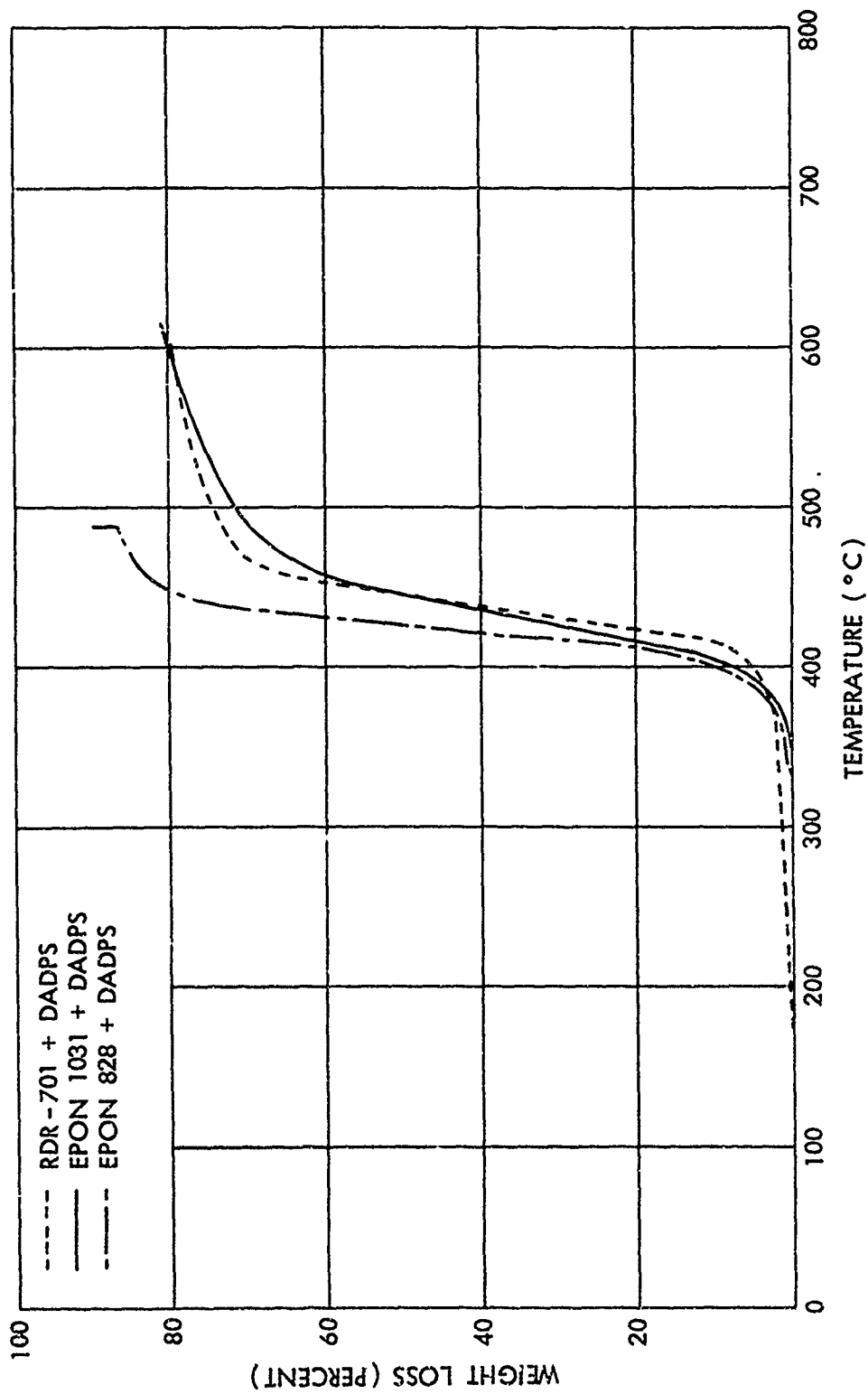


FIG. 12 EFFECT OF DIAMINODIPHENYL SULFONE ON THE THERMAL STABILITY OF SEVERAL EPOXY RESINS

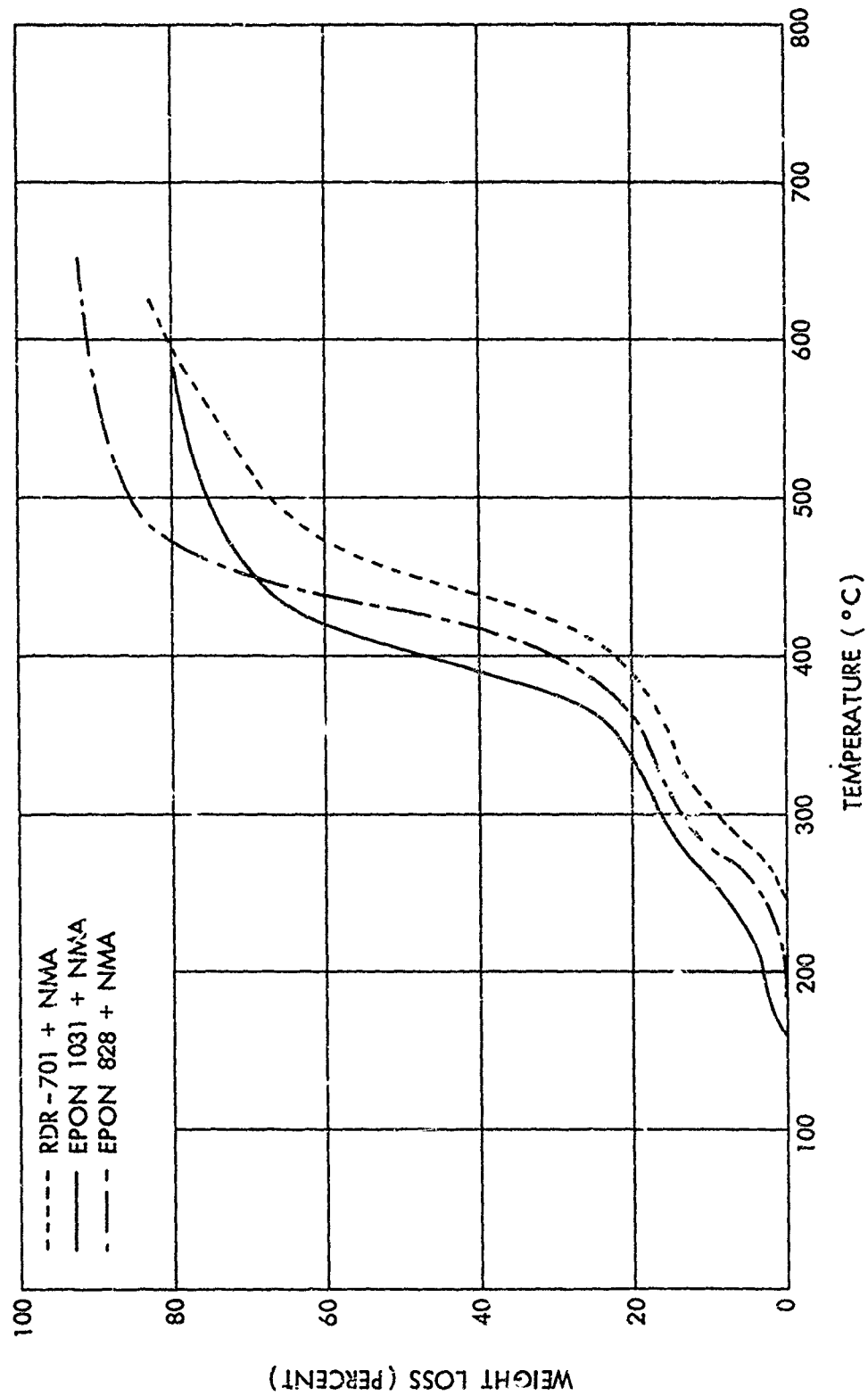
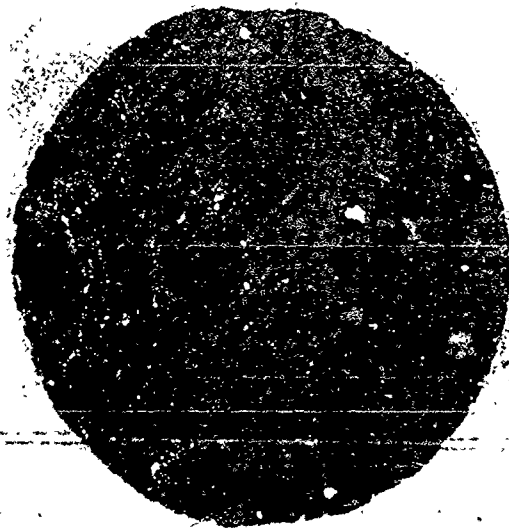
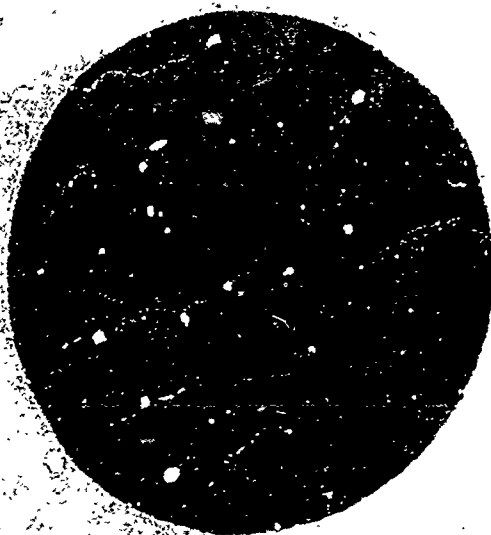


FIG. 13 EFFECT OF NADIC METHYL ANHYDRIDE ON THE THERMAL STABILITY OF SEVERAL EPOXY RESINS

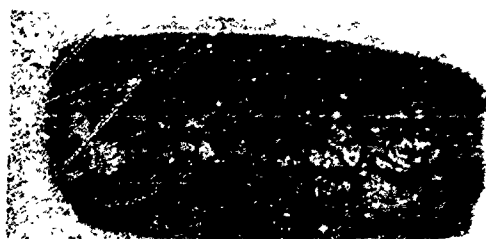
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FRONT VIEW



BACK VIEW

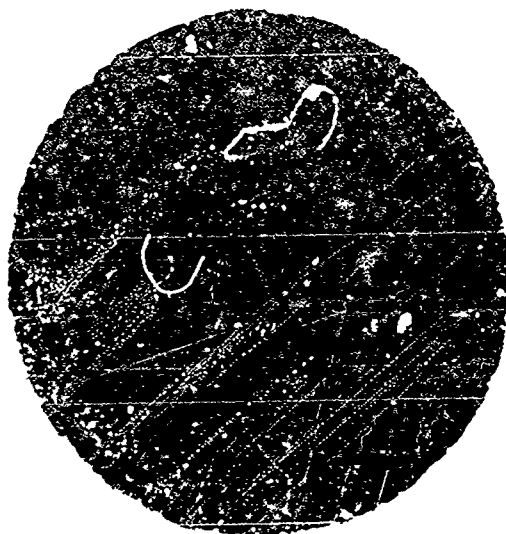


SIDE VIEW

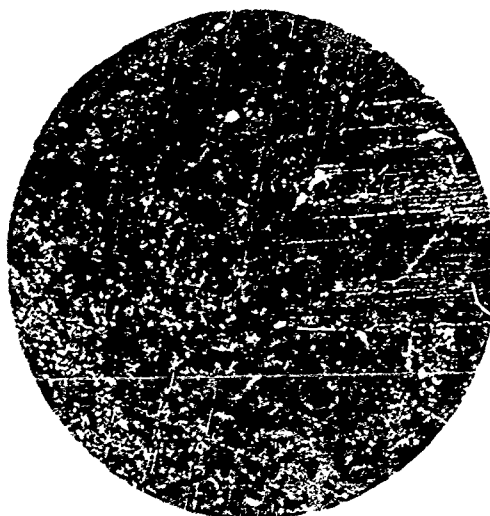
EPON 1031 + NMA + 20% SILICA

FIG. 14 ABLATIVE CHARs AFTER "ALPHA-ROD" TEST

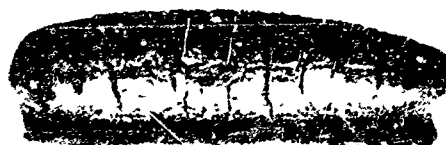
NOLTR 65-50



FRONT VIEW



BACK VIEW



SIDE VIEW

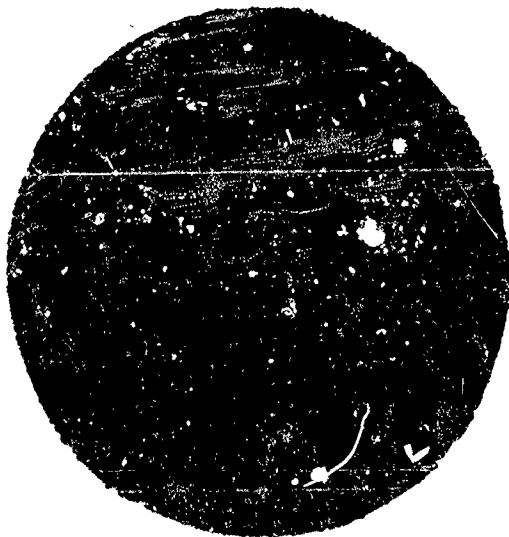
EPON 1031 + NMA + 20% SILICA

FIG. 15 ABLATIVE CHARS AFTER "ALPHA-ROD" TEST

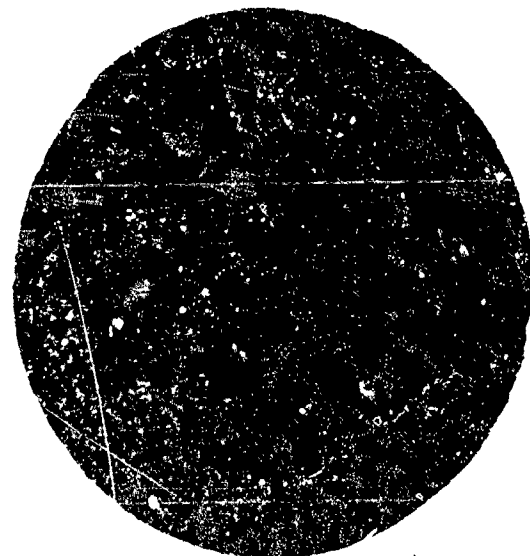
NOLTR 65-50



FRONT VIEW EPON 1031 + NMA.



FRONT VIEW EPON 828 + NMA + 30% SILICA



BACK VIEW EPON 828 + NMA + 30% SILICA

FIG. 16 ABLATIVE CHARS AFTER "ALPHA-ROD" TEST

NOTES 65-50

PHASE I MATERIALS AND STATISTICS

RESIN	CURING AGENT	FILLER	EROSION RATE mils/sec	% CHAR at 550 C	CROSSLINK DENSITY	SPECIFIC GRAVITY
Epon 828	THPA	None	13.8	4.0	60.3	-
Epon 828	THPA	Yes	12.4	-	-	-
Epon 828	TMA	None	10.3	9.0	40.4	-
Epon 828	NMA	None	9.7	11.0	62.2	-
Epon 828	NMA	10%	9.7	-	-	-
Epon 828	NMA	20%	9.7	-	-	-
Epon 828	NMA	30%	<1.2	-	-	1.38
Epon 828	TETA	None	10.1	5.0	37.1	1.19
Epon 828	TETA	Yes	11.1	-	-	1.29
Epon 828	MPDA	None	9.9	11.0	36.6	1.21
Epon 828	MPDA	Yes	10.2	-	-	1.39
Epon 828	DADPS	None	11.3	8.0	36.3	1.24
Epon 828	DADPS	Yes	12.4	-	-	-
Epon 1031	THPA	None	9.8	22.0	46.4	-
Epon 1031	NMA	None	10.9	22.0	97.6	1.26
Epon 1031	NMA	Yes	1.4	-	-	1.35
Epon 1031	DADPS	None	10.8	23.0	32.0	-
RDR-701	DADPS	None	10.1	22.0	4.2	1.33
RDR-701	DADPS	Yes	-	-	-	1.42
RDR-701	NMA	None	10.2	26.0	57.3	1.28
RDR-701	NMA	Yes	2.8	-	-	1.38
RDR-701	MPDA	None	-	25.0	3.7	-
RDR-701	MPDA	Yes	9.9	-	-	-
RDR-701	THPA	None	11.8	14.0	27.9	1.30
Epon 871	TETA	None	-	4.0	51.3	1.03

TABLE 1

NOLTR 65-50

COMPARATIVE TGA DATA
TEMPERATURE VS % WEIGHT LOSS

RESIN SYSTEM	% Weight Loss			
	10%	25%	50%	75%
Epon 828 + NMA	278°	386°	428°	461°
Epon 828 + THPA	367°	406°	426°	448°
Epon 828 + TETA	377°	394°	410°	435°
Epon 828 + TMA	381°	405°	430°	450°
Epon 828 + MPDA	401°	413°	426°	450°
Epon 828 + DADPS	400°	414°	426°	440°
RDR-701 + NMA	305°	408°	426°	555°
RDR-701 + THPA	342°	398°	425°	430°
RDR-701 + MPDA	364°	375°	390°	535°
RDR-701 + DADPS	414°	427°	445°	505°
Epon 1031 + NMA	260°	363°	407°	500°
Epon 1031 + THPA	365°	393°	425°	502°
Epon 1031 + DADPS	404°	422°	445°	528°
Epon 871 + TETA	326°	355°	392°	433°

TABLE 2

NOMER 65-50

COMPARATIVE TGA DATA
WEIGHT LOSS VS TEMPERATURE

RESIN SYSTEM	T e m p. °C		
	350°	400°	450°
Epon 828 + NMA	22%	30%	68%
Epon 828 + THPA	8%	21%	77%
Epon 828 + TMA	5%	20%	75%
Epon 828 + TETA	3%	35%	83%
Epon 828 + MPDA	1%	9%	75%
Epon 828 + DADPS	1%	10%	81%
RDR-701 + NMA	15%	22%	49%
RDR-701 + THPA	10%	26%	73%
RDR-701 + MPDA	2%	60%	71%
RDR-701 + DADPS	2%	6%	56%
Epon 1031 + NMA	22%	45%	69%
Epon 1031 + THPA	5%	31%	65%
Epon 1031 + DADPS	<1%	8%	55%
Epon 871 + TETA	20%	55%	83%

TABLE 3a

WOLTR 65-50

TEMPERATURE RANGE OVER WHICH WEIGHT
LOSSES OF 5 to 75% AND 70 to 80% OCCUR

RESIN SYSTEM	TEMP. RANGE FROM 5.0 to 75.0%	TEMP. RANGE FROM 70.0 to 80.0%
Epon 828 + TMA	100°	10°
Epon 828 + TETA	70°	15°
Epon 828 + THPA	165°	5°
Epon 828 + NMA	200°	25°
Epon 828 + MPDA	55°	25°
Epon 828 + DADPS	50°	10°
RDR-701 + THPA	195°	25°
RDR-701 + NMA	275°	80°
RDR-701 + DADPS	100°	130°
RDR-701 + MPDA	190°	310°
Epon 1031 + NMA	275°	150°
Epon 1031 + DADPS	135°	100°
Epon 1031 + THPA	150°	135°
Epon 871 + TETA	135°	20°

TABLE 3b

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5. AUTHOR(S) (Last name, first name, initial)		
⑬ by Gerald J. Fleming.		
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<p>The work contained in this report encompasses an attempt to correlate the chemical and physical structure of a polymer with its ablative performance. A broad range of epoxy resins and curing agents were employed as model systems. Various tools such as "alpha rod" testing, thermogravimetric analysis, crosslink density studies, and infra-red spectroscopy were used in making this correlation.</p> <p>The epoxy novolac type resin performed the best of all the epoxy resins in the "alpha rod" oxy-acetylene torch test while nadic methyl anhydride performed as the best curing agent for epoxy resins under these ablative conditions. The use of a refractory filler such as SiO₂ was found to be necessary for good performance. The mechanism through which this filler aids the ablative properties of materials is explained with the help of photomicrographs.</p>		

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
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<p>Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 65-50) A CORRELATION OF POLYMERIC STRUCTURE TO ABLIATIVE PROPERTIES, by Gerald J. Fleming. 29 April 1965. 11p. illus., charts, tables. BuWeps task RRMA 03-043/212-1/RO07-04-01.</p> <p>UNCLASSIFIED</p> <p>The work contained in this report encompasses an attempt to correlate the chemical and physical structure of a polymer with its ablative performance. A broad range of epoxy resins and curing agents were employed as model systems. Various tools such as "alpha rod" testing, thermogravimetric analysis, crosslink density studies, and infrared spectroscopy were used in making this correlation.</p>	<ol style="list-style-type: none"> 1. Epoxies 2. Polymers 3. Resins, <p>I. Synthetic Title II. Fleming, Gerald J. III. Project</p> <p>Abstract card is unclassified.</p>	<ol style="list-style-type: none"> 1. Epoxies 2. Polymers 3. Resins, <p>I. Synthetic Title II. Fleming, Gerald J. III. Project</p> <p>Abstract card is unclassified.</p>
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